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Compositional and temperature dependence of elastic constants for $Zn(PO_3)_2$. x Nd_2O_3 glasses

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Abstract : The compositional dependence of the elastic moduli and the attenuation of the longitudinal ultrasonic wave is studied for a series of Nd_2O_3-ZnO- P_2O_5 glasses The density, the ultrasonic wave velocity (longitudinal and shear), the elastic moduli, Poisson's ratio and the ultrasonic attenuation are found to be sensitive to the glass composition The attenuation of ultrasonic compressional waves in the glasses has been measured over the temperature range from room temperature to 534 K. Twin loss peaks in the attenuation against temperature plots at constant frequency were attributed to a relaxation loss of the standard linear solid type. The properties of the high-temperature relaxation processes are found to be rather sensitive to the glass composition It is found from this ultrasonic data, that the present glass system can be divided into "three compositional regions" The room temperature ultrasonic measurements are qualitatively interpreted in terms of changes in the coordination number, the interatomic force constant, and the polarizability of the glass network bonds and cations

Keywords Ultrasonic attenuation, elastic moduli, glasses

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1. Introduction

Phosphate-based glasses are of some interest in commercial applications in optical data transmission, detection, sensing and laser technologies. Metaphosphate glasses are very durable and have other physical properties suitable for laser ion hosts, for example, the spectroscopic properties and possible laser action of Nd^{3+} ion in metaphosphate glasses have been the subject of several studies [1-3].

The structure of phosphate glasses has been studied by measurements of the compositional dependence of the refractive index and optical dispersion [4], electrical conductivity [5-10] and elastic moduli [11-17]. From these studies, one can divide the phosphate glasses into two components, normal and anomalous glasses. In the case of normal glasses, *i.e.*, phosphate glasses containing oxides of Na, Ca, Ba, Cd, and Pb, a number of physical properties change continuously as a function of composition over the entire vitreous range. However, in the anomalous glasses, namely the phosphate glasses containing oxides of Zn, Mg, Mn, Co, Mo, and Bi, the properties show discontinuities at particular composition of the metal oxide. Elastic moduli data of phosphate glasses containing rare-earth materials, are quite rare. However, glasses containing rare-earth ions have considerable potential for application in optical data transmission, detection, sensing and laser technologies; for example, neodymium phosphate glasses have been widely used in lasers [18].

It is pertinent to mention that the velocity and the attenuation of elastic waves at ultrasonic frequencies can be used for the determination of mechanical properties of materials. The ultrasonic pulse, in the MHz range, may cause real displacement of the atoms and / or the molecules from their equilibrium positions as it passes through the sample [19]. Generally, the magnitude of the velocity of an ultrasonic wave travelling in the material is related to its density and one or more elastic stiffness constants. The elastic moduli calculated from the measured ultrasonic wave velocities and densities, at constant temperature, are found to be dependent on the crosslink density, interatomic

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force constants and atomic bond lengths in the material structure [14]. This dependence has been expressed in the form

$$K = \text{constant} \times F / r^n , \quad (1)$$

where K is the bulk modulus, F the bond force constant and r is the diameter of the atomic rings, *i.e.* the smallest closed circuit of atomic bonds. The constant is determined empirically and the power n which is typically high = 4. This model was originally proposed to account for the bulk modulus of the pure vitreous oxides whose ring sizes were assumed to be similar to the ring sizes occurring in the analogous crystal structures and known from X-ray crystallography.

Ultrasonic relaxation phenomena in oxide glasses have been widely studied below room temperature [20-24]. However, investigations at elevated temperatures upto the softening point are rare. At a constant frequency, peaks in the temperature dependence of the attenuation occur which seem attributable to a standard linear solid behavior with low dispersion and Arrhenius relaxation times. Whilst differing from the low-temperature relaxation loss in terms of the order of magnitude of the activation energies and attempt frequencies characterizing the loss. The most interesting feature of the high temperature relaxation phenomenon is the width of the loss peaks, each of which can be understood in terms of the operation of a single relaxation time, *i.e.* there exist discrete relaxation spectra.

The present work forms one part of a programme to explore what information can be obtained about atomic and molecular configurations in glass, from studies of the compositional dependence of the elastic constants of $Zn(PO_3)_2.xNd_2O_3$ glass system. Furthermore, the temperature dependence of attenuation of ultrasonic compressional waves for the same glass series is also highlighted in this study.

2. Experimental technique

2.1 Glass preparation :

Zinc-phosphate glasses containing neodymium were prepared from laboratory reagent grades of Analar phosphorous pentaoxide P_2O_5, zinc oxide ZnO and rare-earth neodymium oxide Nd_2O_3, using alumina crucibles, heated in an electric furnace open to the atmosphere. The reagents were mixed and heated in open alumina crucibles for 1 h at 250 °C. This allows the P_2O_5 to decompose and react with other components before melting would ordinarily occur. After this treatment, the mixture was placed for 1 h in a furnace held at between 950 °C and 1050 °C, the highest temperature being applicable to the mixes richest in Nd_2O_3. The glass melts were stirred occasionally with an alumina rod to ensure homogeneous melts. Each melt was cast into two mild-steel moulds to form glass rods of 1 cm long and 1.6 cm diameter. After casting, each glass was immediately transferred to an annealing furnace held at 300 °C for 1 h. After this, the furnace was switched off and the glasses were allowed to cool to room temperature at an initial cooling rate of 3 °C per minute. This procedure was employed to prepare glass sample of the composition 50 mole % ZnO – 50 mole % P_2O_5 doped with Nd_2O_3 ranging from 0 to 10 wt %. For ultrasonic measurements, samples were cut and polished into the form of cylindrical rods of 1.6 cm diameter and 0.5 cm thickness with parallel faces.

The densities of the samples were measured by the Archimedes method using toluene as the immersion liquid and they are accurate to ± 0.001 gcm^{-3}.

2.2 Ultrasonic measurements :

2.2.1 Room temperature measurements

The ultrasonic compression and shear wave velocity measurements were made by the pulse-echo technique. The ultrasonic waves were generated and received by commercial transducers (longitudinal transducer 4 MHz, 1.6 cm active diameter and shear Krautkramer 4 MHz, 1.3 cm active diameter) actuated by an ultrasonic flaw detector (Ultrasonoscope MI. 32). Details of the technique are presented elsewhere [14].

The elastic constants of the present glass system were calculated at room temperature using the measured densities ρ, longitudinal velocities V_l and shear wave V_s, using the following expression :

longitudinal modulus $$L = \rho V_l^2 , \quad (2)$$

shear modulus $$G = \rho V_s^2 , \quad (3)$$

bulk modulus $$K = L - (4/3)G , \quad (4)$$

Poisson's ratio $$\sigma = \left(V_l^2 - 2V_s^2\right) / 2\left(V_l^2 - V_s^2\right), \quad (5)$$

Young's modulus $$E = (1+\sigma)2G . \quad (6)$$

The procedures of calculating the Debye temperatures are presented elsewhere [16].

2.2.2 High temperature measurements

The specimen holder for the high-temperature measurements is illustrated in Figure 1. This holder was designed to aid the production of exponentially decaying echoes, by means of a device which allowed the contact pressure on the crystal transducer-bond -specimen combination (which are inserted in the space between the two brass buttons) to be varied. This pressure, which was always slight to prevent transducer breakage, was applied by means of a spring *via* a ball and socket joint engaged a contact button resting on the transducer. It could be finely controlled by means of a continuously adjustable clamp, consisting of a large nut on the thread bar which carried the spring and the ball and socket joint. This spring also cushioned the effect brought about by differential thermal contraction or expansion in the sample and the sample holder. All electrically insulating parts of the sample holder (for example, the collars for the rods supporting the contact buttons) were

made of asbestos to permit high-temperature operation. The transducer is coupled to the glass specimen by OV-25 acoustic bond, which is a silicon-based grease supplied by J. J. Chromatographic Ltd.

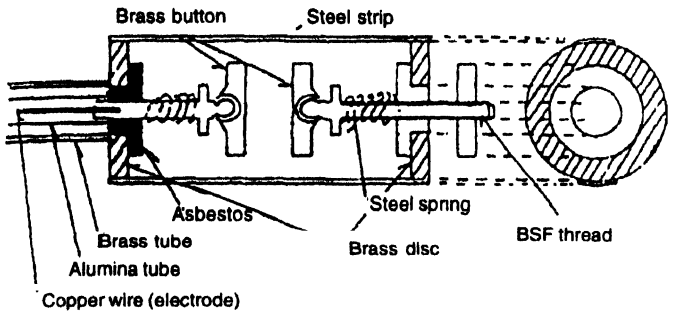

Figure 1. Specimen holder for ultrasonic wave attenuation measurements at high temperature. The ball and socket joints allow ready variation of contact pressure to be made, in order to obtain exponentially decaying echoes

After obtaining the best exponential echo pattern at room temperature, the holder was mounted centrally in a cylindrical furnace. The furnace temperature was controllable from room temperature to 534 K by means of a temperature controller. Temperatures were measured by means of a digital thermometer and a chromel-alumel thermocouple in contact with the middle of the glass rods. The thermocouple leads were protected by alumina sleeves. Ultrasonic attenuation was measured at 10 K intervals increasing from room temperature to 534 K. A quartz transducer (x-cut) of 4 MHz frequency was employed as a common transmitter / receiver. The total maximum error in the measurements of elastic moduli due to changes in specimen thickness (0.02%), velocity (0.05%) and density (0.001%) is therefore about 0.071%.

3. Results and discussion

3.1 Room temperature results :

Table 1 contains the compositions, the densities, the molar volumes, the longitudinal and shear velocities, the elastic moduli, Poisson's ratios, Debye temperatures and the longitudinal ultrasonic wave attenuations for $Zn(PO_3)_2$. xNd_2O_3 glass system. The obtained data in Table 1 have shown that there is a change in behavior of the compositional dependence of all the results around 1 and 4 wt% Nd_2O_3 content.

Reisfeld [25] reported that the rare-earth ions in glasses occupied the center of a distorted cube which is made of four tetrahedra of phosphate glasses. Each tetrahedron contributes two oxygens to the coordination of the rare-earth ions. The overall coordination number is 8, which is the most common coordination number of the rare-earth oxides. According to Reisfeld proposal, the Nd ions may enter the glass network

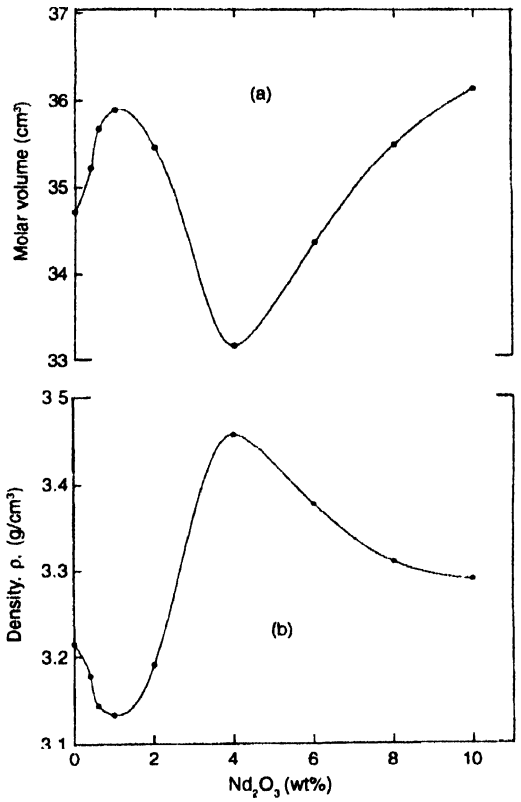

Figure 2. Variations of (a) density and (b) molar volume with Nd_2O_3 wt%

Table 1. Composition, density, molar volume, longitudinal and shear ultrasonic velocities and the elastic constants of $Zn(PO_3)_2$ x Nd_2O_3 glasses at room temperature.

Sample No.	Nd_2O_3 wt%	Density g/cm³	Molar volume cm³	Ultrasonic wave velocity		Elastic moduli (k bar)				Poisson's ratio σ	Debye temp. K	Ultrasonic attenuation α db/cm
				Long V_l m/sec	Shear V_s m/sec	Long L	Shear G	Young's E	Bulk K			
Zn1	0.0	3.215	34.73	4383	2546	618	208	519	340	0.245	452	2.18
Zn2	0.4	3.178	35.22	4263	2483	578	196	487	316	0.243	438	2.45
Zn3	0 6	3.143	35.67	4134	2418	537	184	456	292	0 240	425	2.94
Zn4	1.0	3.132	35.89	3943	2319	487	168	416	262	0.236	407	3.85
Zn5	2.0	3.191	35.46	4378	2540	612	206	513	337	0.246	448	3.08
Zn6	4.0	3.456	33.16	4988	2850	860	281	706	486	0.258	514	1.87
Zn7	6.0	3.377	34.37	4846	2791	793	263	659	442	0.252	497	3.21
Zn8	8.0	3.31	35.5	4611	2665	704	235	587	390	0.249	469	3.80
Zn9	10	3.289	36.14	4317	2520	613	209	519	335	0.242	441	4.42

interstitially. Hence, some network bonds P-O-P or Zn-O-P are broken and replaced by ionic bonds between Nd ion and singly bonded oxygen atoms. So if one assume that the effect of adding Nd cations was only to break down the network bonds P-O-P and Zn-O-P, then an increase in the molar volume with Nd_2O_3 content would be expected for the entire vitreous range of the studied glass system. Experimentally, this effect increases the molar volume in the glass compositional range from 0 to 1 wt% Nd_2O_3 content (see Figure 2(a)) and as a consequence, the values of the density are decreased (see Figure 2(b)). However, in the compositional range from 1 to 4 wt% Nd_2O_3 content, the addition of Nd_2O_3 increased the values of density, which is probably attributable to the simultaneous filling up of the vacancies amidst the network by the interstitial Nd ions with atomic mass 144.24 (*i.e.* increased the packing density) and this will reduce the averaged interatomic spacing, which decreases the molar volume (see Figure 2 (a and b)).

Upon further increase in Nd_2O_3 content beyond 4 wt%, the variation of the glass density is seen to display a decrease up to 10 wt% Nd_2O_3 content. This decrease in density indicates a structural change in the glass network which is accompanied by an increase in the molar volume (see Figure 2 (a and b)).

The addition of Nd_2O_3 to the vitreous $Zn(PO_3)_2$ structure decreases both the longitudinal and the shear wave velocities upto 1wt% neodymium oxide content (see Figure 3 (a and b)). Then beyond 1wt% there is an increase in the ultrasonic wave velocities with further addition of Nd_2O_3 oxide up to 4 wt%. For high Nd_2O_3 percentages *i.e.* > 4 wt%, the ultrasonic wave velocities decrease again (see Figure 3 (a and b)). All the elastic moduli, *viz.* longitudinal, shear, bulk and Young's modulus show the same trend as the ultrasonic wave velocities (see Figure 4 (a and b)). *i.e.* they exhibit the same 3-composition regions behavior that identified in the density, the molar volume and ultrasonic wave velocities for the studied glass system.

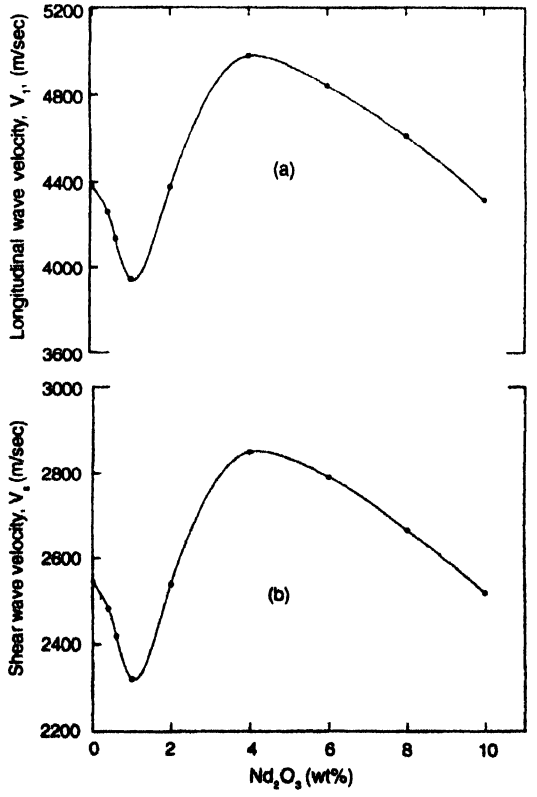

Figure 3. Compositional dependence of (a) longitudinal wave velocity V_l and (b) shear wave velocity V_s.

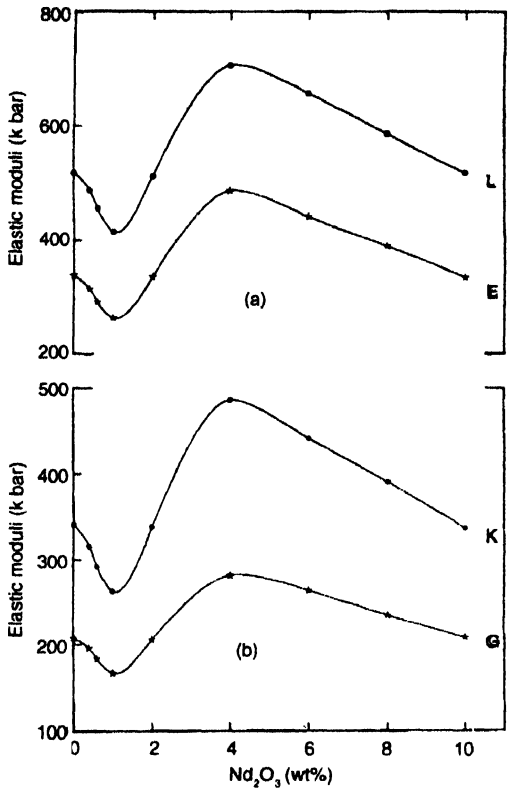

Figure 4. Variations of (a) longitudinal modulus L and Young's modulus E and (b) bulk modulus K and shear modulus G with Nd_2O_3 wt %

The anomalous behavior in the elastic moduli in the present work (Figure 4 (a and b)) may be a result of mere combination of some effects provided by the glass elements with different characters, particularly different coordination numbers, bond strengths, cross-link densities and polarizability of ions. Also it has been reported [26] that in the certain rare-earth elements, the occupation number of the $4F$ shell can take more than one value. This variable valence leads to a rich variety of anomalies in the physical properties of glasses containing these elements. For example, the europium ion size depends strongly on the valence values. The transition of its valence state from 2 to 3 causes a change in the effective ionic radius from 1.17 Å to 0.95 Å, leads to an abrupt contraction in the europium ionic size [27]. Therefore, the anomalous elastic properties of the studied glass system may be ascribed to the variable valence of Nd ions in addition to the structural feature of glass network.

From the above argument, one may expect that the addition of Nd_2O_3 oxide to the vitreous structure $Zn(PO_3)_2$ leads to an increase in cross-link density (cross-link density of P, Zn, and Nd and 2, 2 and 4, respectively), increase in the number of weaker Nd-O ionic bonds compared with P-O bonds (unit bond strength

of P, Zn and Nd are 1.25, 0.50 and 0.50, respectively) and an increase in the polarizability of glasses (polarizability of P, Zn and Nd are 0.05, 0.71 and 1.41, respectively).

According to the expression (1), the decrease in elastic moduli (Figure 4 (a and b)) and the increase in the ultrasonic attenuation α (Figure 5-a) in the first composition region (0-1 wt% Nd_2O_3 content) may be attributed to the increase of the number of weaker Nd-O ionic bonds. However, in the second composition region (1-4 wt% Nd_2O_3 content), substantial increase in elastic moduli and decrease in the ultrasonic attenuation are observed. This is probably attributed to a gradual increase in the cross-link density in glasses due to introduction of Nd ions with coordination number 6. Also the simultaneous filling up of the vacancies amidst the network by the interstitial Nd ions (*i.e.* the increased packing density), this will cause increase in the elastic moduli.

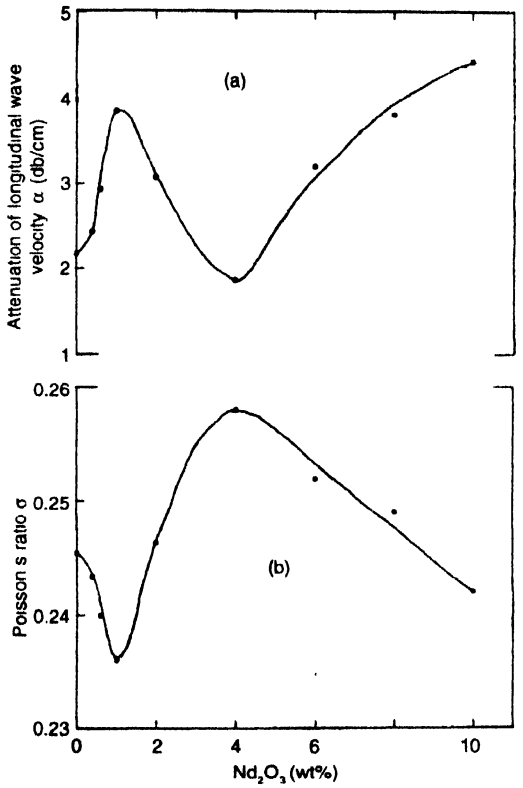

Figure 5. Compositional dependence of (a) ultrasonic attenuation of longitudinal wave velocity α and (b) Poisson's ratio σ.

In the third compositional region (4-10 wt% Nd_2O_3 content), the elastic moduli decrease and the ultrasonic attenuation increases in spite of the fact that the cross-link density and the filling-up of the vacancies of the glass network still increased with the Nd_2O_3 content. This behavior might indicate that there are other opposing processes taking place in this compositional region. From these processes, it is the greater fraction of the weaker Nd-O bonds (when compared with other bonds in the present glass system) which tends to decrease the elastic moduli and increase the ultrasonic attenuation. The other process in the polarizability effect. It has been reported that the modulus of elasticity has shown decreasing effect with increasing polarizability of glasses [28]. So, the pronounced decrease in the elastic moduli and increase in the ultrasonic attenuation in this compositional region may be due to the effect of adding Nd cations with higher polarizability value of 1.41 compared with the polarizability values of 0.05 and 0.71 for P and Zn cations, respectively.

The compositional dependence of Poisson's ratio σ shows the same trend as the elastic moduli (Figure 5-b). To interpret our results on the compositional dependence of Poisson's ratio, we try to isolate the possible variables affecting this parameter and we next consider the relationship.

$$\sigma = (E/2G) - 1. \tag{7}$$

It has been reported [14] that as the cross-link density increased, the value of E or tensile stress applied in the chain direction will remain constant whilst the value of G for shearing force applied parallel to the chains will increase with the cross-link density. Thus, one can argue that Poisson's ratio decreases as the ratio E/G decreases. Also, there is another possible way in which Poisson's ratio might change, is related to the bond force constant. E will increase with bond-stretching force constants, whilst G will increase with bond-bending force constant. Thus, as the ratio of bond-bending force constant to stretching force constant increase, E/G decreases and so Poisson's ratio decreases. According to the above arguments, the variation of Poisson's ratio in the present study may be related to the change in E/G values *i.e.* the change in cross-linking density and bond-bending and stretching force constants. So in the first compositional region of 0-1 wt% Nd_2O_3 content, the ratio E/G showed a decrease from 2.50 to 2.47 (Table 1); this leads to a decrease in the value of Poisson's ratio (Figure 5-b) However, in the second compositional region of 1-4 wt% Nd_2O_3 content, the values of E/G increase from 2.47 to 2.51 and then in the third region of 4-8 wt% Nd_2O_3 content, the values of E/G decrease again from 2.51 to 2.48, this is consistent with the variation of Poisson's ratio in these compositional regions.

The variation of Debye temperature with Nd_2O_3 content (Figure 6) showed the same three compositional regions which

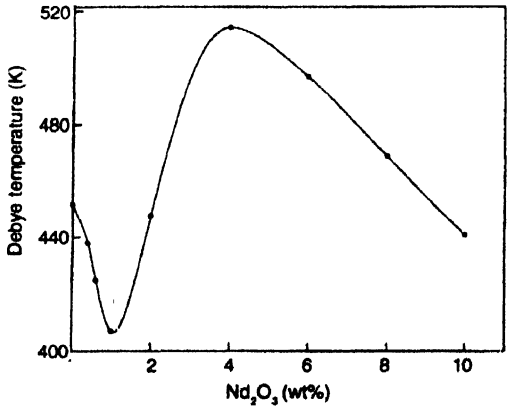

Figure 6. Variations of Debye temperature with Nd_2O_3 wt%.

had been found in the compositional dependence of all the properties studied in the present work.

3.2 High temperature results :

Typical results showing the temperature dependence of the attenuation of ultrasonic compressional waves at 4 MHz are illustrated by data points given in Figure 7 (a-c) for the glasses studied. From the inspection of this figure, we observed that for

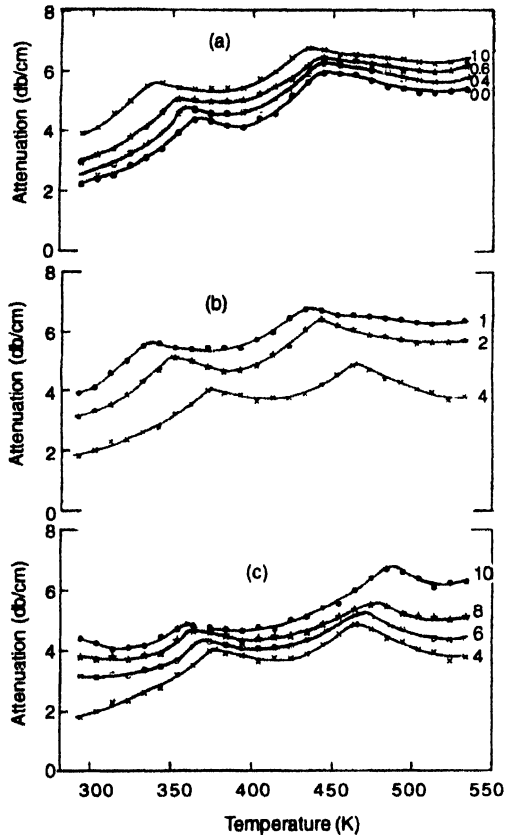

Figure 7. Variations of ultrasonic attenuation of longitudinal wave velocity α with temperature (K).

any glass composition, two loss peaks are obtained, which we shall label R_1 and R_2 for the lower and higher peak temperatures, respectively. Figure 8 (a and b) show that the peak loss and peak temperature are quite sensitive to composition, *i.e.* exhibit the same discontinuity at 1 and 4 wt% Nd_2O_3 that we have found in the composition gradients of other physical properties of the present glass system. Also, we have shown that there are two thermally activated relaxation processes governing the acoustic loss in the studied glasses in the temperature range from 294 to 534 K. Thus, we suggest that the loss originates from particles in two-well systems *i.e.* it could be attributed to a relaxation loss of the standard linear solid type, with low dispersion and two discrete Arrhenius relaxation times [29]. To quantify this suggestion, we need to do some more work on the frequency dependence of the absorption to obtain the activation energies of these two relaxation processes.

4. Conclusions

The room temperature results of the present work led to some understanding of the structure of these rare-earth phosphate glasses. The glass density, the molar volume, the longitudinal and shear wave velocities, the elastic constants and ultrasonic attenuation are found to be sensitive to the additions of the Nd_2O_3 dopant. The present investigated properties revealed structural changes at 1 and 4 wt% of the neodymium oxide content.

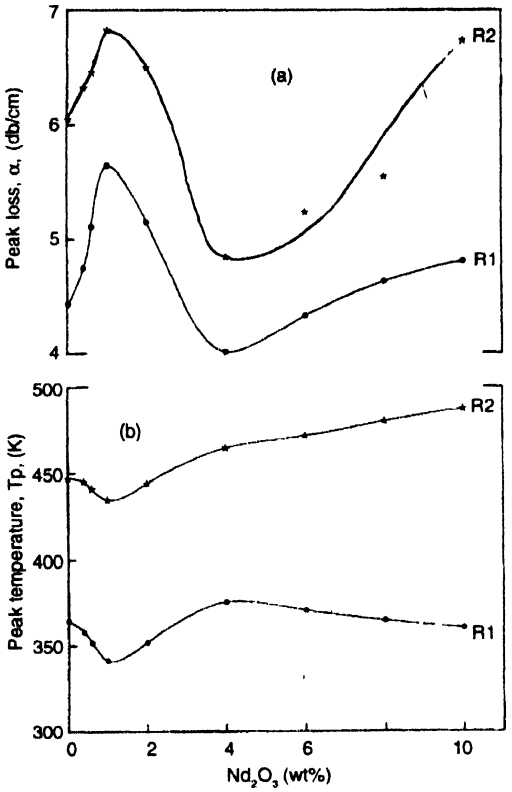

Figure 8. Compositional dependence of (a) peak loss α and (b) peak temperature T_p (K) with Nd_2O_3 wt %.

Also, it is found that two loss peaks due to two relaxation processes are observed in the range of temperature (294 to 534 K) studied. The peak loss and peak temperature are found to be dependent on the composition (Nd_2O_3 wt%). They showed the same compositional behavior observed for the other studied properties. For understanding the nature and origin of these relaxation, more subsidiary work concerning the frequency and temperature dependencies will be carried out in subsequent investigations on these glasses.

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